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Phosphine-catalyzed addition of P(O)–H compounds to ethyl phenylpropiolate

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ABSTRACT

An efficient PBu_3-catalyzed α-addition of the P(O)–H bond to ethyl phenylpropiolate has been developed. This strategy offers a facile method for the preparation of synthetically useful alkenyl phosphonates and phosphinates proceeding under neutral reaction conditions with high atom economy.

Introduction

During the past decades, tertiary phosphines have been recognized as versatile nucleophilic catalysts for a wide variety of synthetically useful transformations of electron-deficient alkenes, allenes, and alkynes.[1] In comparison with nitrogen nucleophiles, tertiary phosphines in many cases show divergent catalytic behavior which mainly results from their stronger nucleophilic properties along with weaker basic character, the ability to play the role of a good leaving group, as well as their unique potential to form ylide-type intermediates. For example, phosphines are known to alter the regioselectivity of nucleophilic addition to electron-deficient alkynes from the Michael-type β-addition to a non-classical α-addition (Scheme 1).

The pioneering work in this field by Trost and Dake[2] introduced nitrogen pronucleophiles at the α-position of propiolate esters using PPh_3 as a catalyst, and was later expanded by Tomita and co-workers who utilized this methodology for oxygen pronucleophiles.[3] More recently, Taran and co-workers reported the first α-addition of phosphorus pronucleophiles; dialkyl phosphites, *H*-phosphinates, and secondary phosphine oxides to alkynes activated by a phosphine oxide moiety in the presence of PBu_3, providing a new strategy to construct pharmacologically active geminal bisphosphonates.[4] However, a limited number of electron-deficient alkynes and nucleophilic reagents have been shown to react with each other to furnish α-addition products.

Inspired by the elegant work of Taran and co-workers[4] we wished to expand the scope of the phosphine-catalyzed α-addition of dialkyl phosphites and *H*-phosphinates using ethyl phenylpropiolate as an electrophilic partner. The resultant multifunctional alkenes (currently accessible by somewhat tedious synthetic procedures) would be useful skeletal motifs for further chemical manipulations aimed at the synthesis of biologically active molecules such as cyclopropane phosphonic acids,[5] thiochomenes,[6] pyrrolizine-3-ones.[7] The presence of an ester group makes the anticipated products readily convertible to phosphonate- and phosphinate-containing carboxylic acids, of which there are many examples presently used as drugs for the treatment of various diseases.[8] Moreover, phosphorylated carboxylic acids attract considerable interest due to their ability to serve as ligands for chelating metal cations.[9]

It is well known that the success of phosphine-catalyzed transformations largely depends on the efficiency of the initial nucleophilic addition of phosphine to the electron-deficient alkene, allene, or alkyne to generate a reactive phosphonium zwitterionic intermediate.[1] Ethyl phenylpropiolate, which is activated by a carbonyl moiety, was expected to react more rapidly with a tertiary phosphine and therefore undergo subsequent α-addition of a dialkyl phosphite or *H*-phosphinate more readily than alkynes bearing a phosphine oxide activating moiety as previously employed by Taran and co-workers.[4] At the same time, the

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